CHARGE PROPERTIES OF SOME CLAYS FROM SOILS WITH VARIABLE CHARGE

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ABSTRACT

The pH-dependence of surface charge density of the clay fraction of five horizons of a variable-charge soil has been studied by adsorption of potential-determining ions (p.d.i.) and by adsorption of electrolyte ions. In samples with a high proportion of clay minerals (mainly illite) it is not possible to reach the point of zero charge, but samples with lower contents in clay minerals and a higher proportion of metal oxides show a well-defined PZC. Adsorption of p.d.i. by those samples with a low content of clay minerals can be satisfactorily described by a model which considers a three - plane distribution of the electric potential. Some deviations found at acid pH values can be explained by the presence of minerals with a permanent negative charge. Results for adsorption of electrolyte ions are also consistent with the presence of permanent charge.

INTRODUCTION

Constant surface charge, mainly due to the permanent charge of clay minerals, usually predominates in most soils from temperate regions, while in many soils from the tropics a pH-dependent charge prevails, so that the surface electric potential is largely, but not exclusively, determined by the concentration of H^+ or OH^- in solution. This electric potential is usually assumed to be determined by the Nernst relationship (Van Raij and Peech, 1972; Keng and Uehara, 1973; Laverdiere and Weaver, 1977; Parker et al., 1979; Uehara and Gillman, 1980). This assumption is not rigorous, as it implies that the activity of potential-determining ions (p.d.i.), H^+ and OH^-, on the surface is independent of the pH of the solution. A detailed description of the implications of the Nernst equation is given by Bowden et al. (1977).

The use of the Nernst equation and of erroneous versions of the Stern model make some modern studies of charge properties of soils

with variable charge of questionable value (Madrid, 1980).

In this paper the model of three potential planes described by Barrow et al. (1980) is used to describe some charge properties of a soil from South Western Spain, which, unlike most mediterranean soils, shows variable charge properties. This model, which contains a number of parameters which are determined essentially by curve-fitting procedures, represents a realistic approach inasmuch as the simultaneous variation of all variables involved is considered, and its applicability has been demonstrated for various adsorbents and experimental conditions (Barrow et al., 1980; Madrid et al., 1981).

EXPERIMENTAL

Clays

The samples studied are clay fractions of five horizons of a ferritic brown earth (Eutrochrepts from Los Marines, South Western Spain). Some relevant properties of the soils are given in Table 1, and the approximate composition of the clay fractions are given in Table 2 (Sociedad Española de Ciencia del Suelo, 1966).

TABLE 1

Some properties of the soils

Sample	Horizon	Depth cm	pH KCl	SiO_2	Al_2O_3	Fe_2O_3	MgO	Clay
				per cent				
1	A_0A_1	0-30	6.0	27	29	25	2	8
2	A_1	30-60	6.3	23	31	26	2	7
3	IIAB	60-90	6.5	16	40	26	2	22
4	IIB_{11}	90-120	6.4	17	39	25	2	24
5	IIB_{12}	120-150	6.2	13	40	26	2	20

Adsorption of potential-determining ions

Volumes of 0.05N HCl or NaOH were added to polythene bottles containing suspensions of 0.1 g of clay in 20 ml of 0.01, 0.1 or 1M NaCl solutions, while flushing wet CO_2-free N_2 gas purified as described by Evans (1976) through the suspensions. Volumes of titrant were chosen so that pH readings ranged from 3.5 to 10.5. The bottles were sealed air-tight while in N_2 atmosphere and after shaking for 1 hour pH was measured. Similar treatments were carried out with 20-ml samples of the appropriate NaCl solutions (blanks). Up-

take of H^+ (or OH^-) by the clay was calculated from differences between titrant volumes added to test and blank samples at each pH. The value obtained was considered equal to the amount of positive (or negative) charges on the surface.

TABLE 2

Composition of the clay fractions

Sample	Illite	Goethite	Gibbsite	Amorphous	Other clay minerals
1	++	+++	++	+	None
2	++	+++	++	-	None
3	+	+++	+++	+	None
4	+	+++	+++	++	None
5	+	+++	+++	+++	None

+++ Abundant
++ Scarce
+ Present

The common point of intersection of curves obtained at different ionic strengths was considered the point of zero charge (PZC). The net surface charge density at each pH was calculated by subtracting from the uptake of H^+ or OH^- the value corresponding to the PZC, and dividing by the BET specific surface area determined by N_2 adsorption on the samples pretreated at 10^{-6} torr and room temperature for 24 hours. About 30 points were obtained for each curve of adsorption of p.d.i.

Adsorption of electrolyte ions

Adsorption of Na^+ and Cl^- ions was measured at three pH values (i.e. 4, 7 and 10) and two ionic strengths (i.e. 0.1M NaCl and 0.01 M NaCl) by the method of Van Raij and Peech (1972). When the electrolyte was 1M NaCl, the entrained solution caused large errors in the determination of adsorbed ions, so that no results are shown here for this ionic strength. All these experiments were done in duplicate.

DISCUSSION

Figures 1, 2 and 3 show the variation of the electric surface charge with pH for samples 3, 4 and 5. Full lines indicate measurements of adsorption of p.d.i. and crosses and circles those of electrolyte ions in 0.01 and 0.1M NaCl respectively. The results show a well-defined PZC (crossover point) at pH values which are in good agreement with PZC values of pure aluminium and iron oxides (Parks, 1965; Cabrera, 1975; Madrid et al., 1981). On the other hand, samples 1 and 2, with higher contents in SiO_2 and illite (Tables 1 and 2), gave curves of adsorption of p.d.i. which did not cross within the studied pH range (not shown). They seemed to converge towards very acid pH values, so that even though no PZC could be defined, both samples seem to have their PZC at pH below 2. This behaviour of samples 1 and 2 may be due to a higher proportion of minerals with a permanent charge, primarily illite.

When the set of equations given by Barrow et al. (1980) is solved for data of samples 3, 4 and 5, dashed lines of Figures 1, 2 and 3 are obtained. As can be seen, the basic side of the curves of adsorption of p.d.i. of these three samples can be fitted by the model, but important deviations are found on the acid side. As these samples also contain some illite, its permanent charge can have some influence on the results. This influence would be less noticeable when the variable-charge surfaces were also negative, but when these surfaces are uncharged or positively charged the heterogeneous distribution of charge would cause a definite deviation of the behaviour of the sample from that described by the model. The presence of permanent charge makes the estimated values of the parameters of the model less reliable than if only variable charges were present, as the parameters relate to an "average" surface. Therefore the information in Table 3 is only given for orientative purposes.

Results for K_H are about one order of magnitude lower than those obtained for pure iron oxides (Madrid et al., 1981). As silicate surfaces are known to show less affinity for H^+ ions than iron or aluminium oxide surfaces (Bowden, 1973), this result can be explained by the contribution of the clay minerals to the "average" surface. On the other hand, values of K_{OH} are of the same order of magnitude as those found for pure iron oxides (Madrid et al., 1981).

Results for ion adsorption (Figures 1, 2 and 3, crosses and circles) at pH 4 and 7 seem to indicate that the charge is more negative (or less positive) than that measured by adsorption of p.d.i. This could again be explained by the presence of permanent negative charge on sites of the illite not accesible to H^+ ions. Part of

this permanent charge could become accesible to the ions in solution during the period of treatment and measurement, if the technique used could cause alteracion of the mineral. However, experiments at pH 10 do not show any difference between adsorption of p.d.i. and electrolyte ions. This observation could be explained by the higher stability of the mineral at alkaline pH values. It has been demonstrated that the illite contained in these samples is easily altered at acid pH (J.L. Pérez, personal communication, 1981).

TABLE 3

Estimated values of some parameters of the model of three planes of potential

Sample	R^2	$N_s \times 10^9$	$K_H \times 10^{-7}$	$K_{OH} \times 10^{-7}$	K_{Na}	K_{Cl}
3	0.98	1.7	4.00	10.08	0.40	0.30
4	0.98	2.0	0.11	1.83	0.04	0.80
5	0.97	4.3	0.13	4.35	0.01	0.30

R^2, fraction of the sum of squares accounted for by the model
N_s, maximum number of sites, eq x cm^{-2}
K_H, K_{OH}, K_{Na} and K_{Cl}, binding constant between each ionic species and the surface, l x mol^{-1}

In summary, the general trend of the variation of the electric surface charge with pH of these soil clays seems to be largely determined by their high content of minerals with variable-charge surfaces (iron and aluminium oxides), but the presence of minerals with a permanent charge should be considered when explaining the particular data, even for samples of those horizons where clay minerals are present in lower proportions.

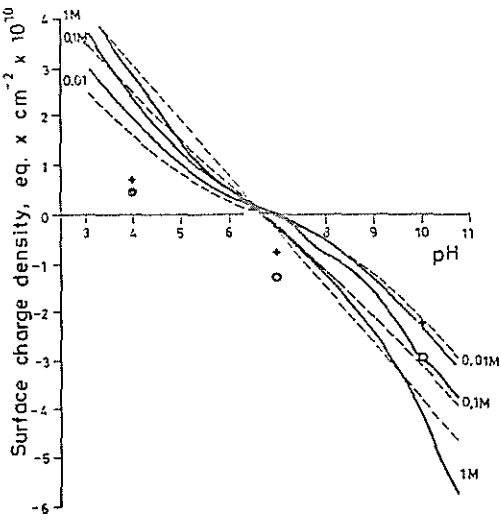

Fig. 1. Variation of surface charge of sample 3 with pH. See text for explanation of the symbols.

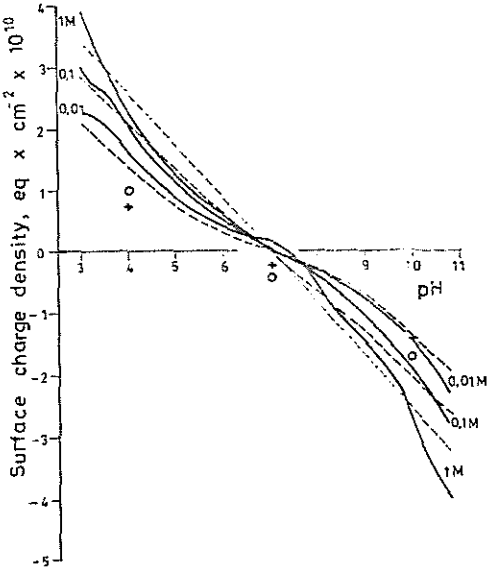

Fig. 2. Variation of surface charge of sample 4 with pH. See text for explanation of the symbols.

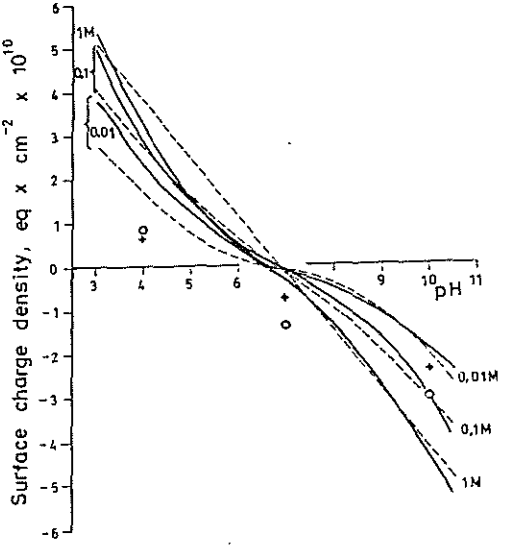

Fig. 3. Variation of surface charge of sample 5 with pH. See text for explanation of the symbols.

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